

JP 5600289.7

(12) UK Patent Application (19) GB (11) 2 054 548 A

- (21) Application No 8019901
(22) Date of filing 18 Jun 1980
(30) Priority data
(31) 54/077756
54/093264
54/096681
(32) 19 Jun 1979
24 Jul 1979
31 Jul 1979
(33) Japan (JP)
(43) Application published
18 Feb 1981
(51) INT CL³
C23F 11/12
(52) Domestic classification
C1C 230 232 233 23X 324
405 B
(56) Documents cited
GB 2026517A
GB 1414918
GB 772775
(58) Field of search
C1C
(71) Applicants
Kurita Water Industries
Ltd.,
No. 15-1, Kitahama
2-chome,
Higashi-ku,
Osaka-shi,
Osaka,
Japan.
Sanyo Chemical
Industries Ltd.,
No 11-1
Ichinohashinomotocho,
Higashiyama-ku,
Kyoto-shi,
Kyoto,
Japan.
(72) Inventors
Kenji Kobayashi,
Masaru Okamoto,
Fumio Kawamura,
Toshiro Rukuda,
Yoshimi Inden,
Jiro Yamamoto.
(74) Agents
Gill Jennings & Every,
53/64 Chancery Lane,
London WC2A 1HN.

(54) Scale removal

(57) A method of removing scale deposited on a surface in contact with water, which comprises adding to the water a descaling agent comprising an itaconic acid polymer derived from 75 to 100 mol % itaconic acid and 0 to 25 mol% of another unsaturated monomer.

*itaconic
acid*

GB 2 054 548 A

SPECIFICATION

Scale removal

- 5 The present invention relates to a method of removing scale deposited in a water system such as a boiler or water cooler. Thermal efficiency is often reduced and local corrosion is often brought about in a water system, particularly on heating surfaces therein, owing to the deposition of scale and/or sludge. The deposition is a result of the fact that impurities such as calcium, magnesium and silica are contained in water. Consequently, for example, calcium carbonate, hydroxyapatite and/or magnesium silicate are deposited on surfaces, especially heating surfaces, coming into contact with water. 10
- Medium and low pressure boilers have recently been produced, having good performance properties, whose unit heating surface evaporation rate and fire furnace thermal load are very high in comparison with those of conventional boilers. As a result of the increased thermal load on heating surfaces, the impurities in the water used are more highly concentrated, causing increased scale deposition as well as the problem that a small degree of scale deposition may cause expansion and bursting of evaporation tubes. 15
- Most of the scale is caused by substances, such as calcium carbonate, hydroxyapatite, magnesium silicate and iron oxide, which are soluble in inorganic acids such as hydrochloric acid and sulfuric acid. Accordingly the removal of scale has been effected by stopping operation of a boiler temporarily, allowing or causing the temperature to fall, and cleaning the boiler with an inorganic acid. However, the stoppages and the reactivity, danger in handling and problems in safe discharge, after cleaning, of the acid, are serious disadvantages. 20
- It has been proposed to use a chelating agent such as nitrilotriacetate, though inferior in scale solubilisation to inorganic acids, as a descalant, in order to avoid the above disadvantages. However, such chelating agents give off offensive vapour, corrode metal, and render boiler operation control difficult, still without avoiding the temporary stoppages. 25
- It has recently been proposed to use polyacrylates which are capable of removing scale without stopping the boiler operation. However, while such polyacrylates have a certain effect in the removal of scale composed mainly of calcium carbonate and/or calcium silicate, they have scarcely any effect in the removal of scale, most frequently produced in boilers, composed mainly of hydroxyapatite. 30
- According to the present invention, a method of removing scale deposited on a surface contacted with water comprises adding to the water a polymer derived from 75 to 100 mol% of itaconic acid and 0 to 25 mol% of another unsaturated monomer.
- The polymer used in the invention is a homopolymer or copolymer of itaconic acid or its anhydride or a water-soluble salt thereof. In suitable copolymers, examples of unsaturated monomers are unsaturated carboxylic acids and their anhydrides, for example, monoethylenically unsaturated homo- or poly-carboxylic acids such as acrylic acid or methacrylic acid, maleic acid, maleic anhydride or fumaric acid; unsaturated sulfonic acids, which may be aliphatic or aromatic, such as vinylsulfonic acid, allylsulfonic acid, vinyltoluenesulfonic acid, or styrenesulfonic acid; (meth)acrylicsulfonic acids such as sulfopropyl (meth)acrylate or 2-hydroxy-3-(meth)acryloxypropylsulfonic acid; hydroxy group-containing monomers, for example, monoethylenically unsaturated alcohols such as (meth)allyl alcohol, monoethylenically unsaturated ethers or esters of polyols such as alkylene glycols, glycerol or polyoxyalkylene polyols, hydroxyalkyl (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, triethylene glycol (meth)acrylate or hydroxyethyl itaconate, or polyethylene glycol mono-(meth)allyl ether; amide group-containing monomers, for example, (meth)acrylamide, N-alkyl(meth)acrylamides such as N-methylacrylamide or N-hexylacrylamide, N,N-dialkyl(meth)acrylamides such as N,N-dimethylacrylamide, N,N-di-n-propylacrylamide, N-hydroxyalkyl(meth)acrylamides such as N-methylol(meth)acrylamide or N-hydroxyethyl(meth)acrylamide, N,N-dihydroxyalkyl(meth)acrylamides such as N,N-dihydroxyethyl(meth)acrylamide, or vinyl lactams such as N-vinyl-pyrrolidone; unsaturated carboxylic acid esters, for example, C₁₋₁₈ alkyl esters of monoethylenically unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid, fumaric acid or itaconic acid, e.g. methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate or 2-ethylhexyl (meth)acrylate; esters of monoethylenically unsaturated alcohols, for example, vinyl esters or (meth)allyl esters, such as vinyl acetate or (meth)allyl acetate; unsaturated nitriles such as acrylonitrile; and aromatic vinyl compounds such as styrene. The unsaturated carboxylic acids and unsaturated sulfonic acids are preferred. Vinylsulfonic acid, styrenesulfonic acid, (meth)acrylic acid, maleic acid and maleic anhydride are particularly preferred comonomers. 55
- The amount of the itaconic acid in the polymer, when any unsaturated comonomer is an unsaturated carboxylic acid, is preferably at least 80 mol% and more preferably at least 90 mol%, the balance being the comonomer. When any unsaturated comonomer is other than an unsaturated carboxylic acid, the amount of the itaconic acid is preferably more than 90 mol%, more preferably at least 91 mol% and most preferably at least 95 mol%, the balance being the comonomer. When any comonomer comprises a mixture of unsaturated carboxylic acid and other unsaturated monomer, the total amount is preferably less than 10 mol%. 60
- The molecular weight of the itaconic acid polymer used in the present invention is usually from 1,000 to 200,000, preferably 3,000 to 50,000.
- The itaconic acid polymer can be obtained, for instance, by polymerising itaconic acid and any 65

comonomer, usually at a temperature of 40 to 150°C, preferably 50 to 90°C, in the presence of a conventional polymerisation initiator which may be of the peroxide type, e.g. benzoyl peroxide, of the azo type, e.g. azobisisobutyronitrile, or of the persulfate type, e.g. sodium persulfate. The polymerisation method can be conventional, such as polymerisation in aqueous solution.

- 5 The itaconic acid polymer used in the present invention may be in the form of a water-soluble salt, e.g. an alkali metal (such as sodium, potassium, or lithium) salt, an ammonium salt, an amine (such as triethanolamine) salt, or a mixed salt. Alkali metal salts are preferred. Such a water-soluble salt may be prepared either by polymerising a monomer salt or by transforming the polymerised monomer(s) into a salt. Water-soluble salts of the itaconic acid polymer are preferred to the non-salt form of the polymer. 5
- 10 The scale removal method of the present invention may involve the use of the itaconic acid polymer alone, but better results can be achieved by the concurrent use of an acrylic polymer (or a water-soluble salt thereof). Suitable acrylic polymers include homopolymers and copolymers of (meth)acrylic acid or a water-soluble salt thereof. Monomers which may be copolymerised with the (meth)acrylic acid are similar to the unsaturated comonomers described above for forming into copolymers with itaconic acid. The molar 10
- 15 ratio of (meth)acrylic acid to any other monomer is not critical but the amount of (meth)acrylic acid (or its water-soluble salt) is normally more than 50 mol%, and preferably more than 70 mol%, based on the acrylic polymer. The acrylic polymer normally has a molecular weight of from 1,000 to 100,000, and preferably of from 2,000 to 50,000. If the acrylic polymer is used in salt form, that salt may be of the same type as described above for the itaconic acid polymer, and is preferably an alkali metal salt. 15
- 20 The amount of descaling agent which is used in the invention depends on the nature, composition and amount of the deposited scale, but, generally speaking, it is from 1 to 100 mg/l. 20
- The weight ratio of the itaconic acid polymer to any acrylic polymer depends on the composition of the deposited scale and, in particular, the amounts of calcium carbonate and hydroxyapatite, but, generally speaking, is 100:5 - 1000, preferably 100:10 - 200, and more preferably 100:20 - 50. Cost can be reduced, 25
- 25 without lowering operation efficiency, when the amount of any acrylic polymer is from 5 to 1000 parts by weight. The amount of the itaconic acid in the sum of the itaconic acid polymer and an acrylic polymer is normally at least 20 mol% and is preferably from 40 to 90 mol%. 25
- When an itaconic acid polymer and an acrylic polymer are used, they may be compounded before use, and then added to the water system being treated together, or they may be added separately, in suitable 30
- 30 amounts. 30
- Systems which can be treated by the method of the invention include those wherein scale is generated, such as water boilers, water cooling circulation systems, saline water evaporators, waste liquid concentration systems, and exhaust gas dust collecting water systems. The novel method is most suitable for the treatment of systems including heating surfaces such as boiler systems.
- 35 The scale removal method according to the present invention is suitably carried out by treating scale which has been deposited to a degree in excess of an allowable limit, i.e. when the system to be treated needs cleaning. The water-contacting surfaces of the system are treated at an elevated temperature, for instance, at the plant operation temperature with the descaling agent used in the present invention added to the water. 35
- 40 When the scale removal method according to the present invention is used to treat, say, boiler scale, the boiler operation may be stopped temporarily, the scale then being removed in conventional manner. However, it is an advantage of the method of the present invention that boiler scale removal can be effected without stopping the boiler operation. In other words, when an operating boiler needs cleaning, the descaling agent can be added to the boiler feedwater for a given period of time while continuing operation. The 40
- 45 resultant vapour can be absolutely free from odours caused by chemicals and scale composed mainly of, for example, calcium carbonate, iron oxide, calcium silicate and/or hydroxyapatite can be removed to the full. The removed scale is discharged outside the system, together with water. 45
- The time at which the descaling agent used in the present invention is added depends, for example, on the kind of plant. Preferably, however, it is added when scale deposits are 0.01 mm or more, e.g. 0.05 to 0.5 mm, 50
- 50 in thickness. 50
- The temperature at which the treatment with the descaling agent is conducted is normally the plant operation temperature, e.g. 10 to 200°C but may be different from that temperature when the plant is stopped for descaling. The period required for treatment depends on the treatment temperature and the amount of scale deposited, but is normally from 10 to 60 days.
- 55 Ordinarily, boilers are cleaned once a year, and this is also suitable for use of the method of the present invention. Preferably, scale removal is carried out more frequently, for instance, once a month or once in several months. This is because the method is more effective in removing a small amount of scale. Descaling may be conducted prior to the periodical boiler repair. The same is true for the removal of scale generated in, say, a cooling water system. 55
- 60 The scale removal method according to the present invention can be used for the removal of scale generated in a water system which has been operated with or without using any scale inhibitor. Scale inhibitors which may have been used include acrylic polymers, phosphoric compounds and polyvalent metal compound ionisable in water (of the type disclosed in German Offenlegungsschrift No 2,643,533); maleic polymers (e.g. of the types disclosed in British Patent Specifications Nos 772,775 and 1,414,914 and in 65
- 65 U.S. Patent Specification No 2,723,956); and amide polymers (e.g. of the types disclosed in U.S. Patent 65

Specifications Nos 3,928,186 and 3,692,673).

The scale removal method according to the present invention can be operated with the concurrent use of chemicals conventionally used in boilers and cooling water systems, for instance, alkaline agents such as sodium hydroxide, potassium hydroxide, morpholine or cyclohexylamine, corrosion inhibitors such as phosphates, hydrazine, triethanolamine, organic acid salts, chelating agents such as ethylenediaminetetra-
5 acetic acid, and bactericides such as hypochlorous acid.

Of the following, Examples 4 to 8, 11, 14, 15, 18, 21, 22, 25, 28 to 34, 38 to 42, 45, 48, 49, 52, 53 and 56 to 64 illustrate the present invention while Examples 1, 2, 3, 9, 10, 12, 13, 16, 17, 19, 20, 23, 24, 26, 27, 35, 36, 37, 43, 44, 46, 47, 50, 51, 54 and 55 are comparative.

10

Examples 1 to 34

An internally heated autoclave equipped with a vapour outlet port, a water supply port and an electric heater tube was operated for 3 days under a concentration multiple of 10 and a pressure of 10 kg/cm², while supplying Yokohama tap water containing 200 mg/l sodium hydroxide. The pH of the water within the
15 autoclave was maintained at 11.5 - 11.7.

The heater tube was taken out, after 3 days, for observation. The whole surface of the tube was covered with hard scale comprising 65% calcium carbonate, 15% calcium silicate and 8% magnesium silicate.

Next, the plant was operated for 2 days by using softened Yokohama tap water and continuously adding 100 mg/l of various descaling agents in turn. The agents which were used are shown in Tables 1 to 3. The
20 scale removal rate (x) was determined from the amounts of scale removed (y) and deposited (z) from the following formula:

$$x = 100 y / z \%$$

25 Table 1 shows the results obtained in comparative experiments and from itaconic acid homopolymers; Table 2 shows the results obtained from itaconic acid copolymers; and Table 3 shows the results obtained from the concurrent use of itaconic acid type polymers and acrylic polymers. In Table 3, the figures given in the "Descaling agent" column in brackets, e.g. (90), indicate the proportion of the given monomer in the copolymer and the ratio given after the = sign indicates the molar ratio of the two polymers.

25

TABLE 1

Example	Descaling agent	Amount of scale deposited (g)	Amount of scale removed (g)	Scale removal rate (%)
1	None	7.25	-	-
2	Sodium triphosphate	7.12	0.07	0.98
3	Sodium polyacrylate (molecular weight 4,500)	7.31	5.50	75.2
4	Itaconic acid homopolymer (molecular weight 2,000)	7.38	5.70	77.2
5	Itaconic acid homopolymer (molecular weight 3,000)	7.19	6.85	95.3
6	Itaconic acid homopolymer (molecular weight 4,500)	7.23	7.22	99.9
7	Itaconic acid homopolymer (molecular weight 50,000)	7.29	6.91	94.8
8	Itaconic acid homopolymer (molecular weight 100,000)	7.34	5.58	76.0

TABLE 2

Example	Descaling agent		mol% (a) : (b)	Amount of scale deposited (g)	Amount of scale removed (g)	Scale removal rate (%)
	Monomer (a)	Monomer (b)				
9	Itaconic acid	Maleic anhydride	25 : 75	7.18	3.76	52.4
10			50 : 50	7.09	3.55	50.1
11			75 : 25	7.15	6.87	96.1
12	Itaconic acid	Vinyl acetate	25 : 75	7.20	2.52	35.0
13			50 : 50	7.24	4.08	56.3
14			75 : 25	7.26	6.27	86.4
15			91 : 9	7.40	7.35	99.3
16	Itaconic acid	Acrylamide	25 : 75	7.19	2.31	32.1
17			50 : 50	7.11	3.4	47.9
18			75 : 25	7.18	6.31	87.9
19	Itaconic acid	Acrylic acid	25 : 75	7.30	3.72	51.0
20			50 : 50	7.25	3.90	53.8
21			75 : 25	7.19	7.11	98.9
22			90 : 10	7.20	7.20	100.0
23	Itaconic acid	Styrene	25 : 75	7.19	2.24	31.2
24			50 : 50	7.08	3.23	45.6
25			75 : 25	7.27	6.38	87.8
26	Itaconic acid	Styrenesulfonic acid	25 : 75	7.19	2.96	41.2
27			50 : 50	7.18	3.73	51.9
28			75 : 25	7.22	6.99	96.8
29			91 : 9	7.20	7.20	100.0

TABLE 3

Example	Descaling agent	Amount of scale deposited (g)	Amount of Scale removed (g)	Scale removal rate (%)
30	Itaconic acid homopolymer (molecular weight 4,500) (I): sodium polyacrylate (molecular weight 4,500) (II) = 3 : 1	7.38	7.30	98.9
31	(I) : (II) = 1 : 1	7.26	6.47	89.1
32	(I) : acrylic acid(90) - methacrylic acid(10)copolymer (molecular weight 10,000) = 3 : 1	7.19	6.94	96.5
33	Itaconic acid(95)-acrylic acid(5)copolymer (molecular weight 6,000) (I') : (II) = 3 : 1	7.41	7.39	99.7
34	(I') : (II) = 2 : 1	7.19	6.89	95.8

Examples 35 to 62

The procedure of Examples 1 to 15, 19 to 22 and 26 to 34, respectively, was repeated, except that 100 mg/l of trisodium phosphate was added to the water. The hard scale which was generated in this instance was observed to comprise 67% hydroxyapatite, 13% magnesium silicate and so forth.

- 5 It will be evident from the results shown in Tables 4 to 6 (respectively corresponding to Tables 1 to 3) that the conventional sodium polyacrylate is almost ineffective in removing scale of the hydroxyapatite type, 5 whilst a suitable itaconic acid polymer can achieved a satisfactory scale removal rate.

In Examples 61 and 62, the itaconic acid copolymer was different from that in Examples 33 and 34 in that it comprised itaconic acid (90, not 95) and acrylic acid (10, not 5). The molecular weight was still 6000.

TABLE 4

Example	Descaling Agent of Example	Amount of scale deposited (g)	Amount of scale removed (g)	Scale removal rate (%)
35	None	2.88	-	-
36	2	2.75	0.01	0.4
37	3	2.64	0.40	15.2
38	4	3.04	1.18	38.8
39	5	2.75	2.18	79.3
40	6	3.04	2.48	81.6
41	7	3.12	2.33	74.7
42	8	2.75	1.01	36.7

TABLE 5

Example	Descaling Agent of Example	Amount of scale deposited (g)	Amount of scale removed (g)	Scale removal rate (%)
43	9	2.98	0.75	25.2
44	10	2.94	0.84	28.6
45	11	2.98	2.29	76.8
46	12	2.82	0.31	11.0
47	13	2.91	0.45	15.5
48	14	2.96	2.10	70.9
49	15	3.02	2.44	80.8
50	19	3.19	0.48	15.0
51	20	3.00	0.54	18.0
52	21	2.97	2.32	78.1
53	22	3.11	2.80	90.0
54	26	3.02	0.41	13.6
55	27	2.90	0.48	16.6
56	28	2.91	2.25	77.3
57	29	2.83	2.53	89.4

TABLE 6

Example	Descaling Agent of Example	Amount of scale deposited (g)	Amount of scale removed (g)	Scale removal rate (%)	
58	30	2.61	2.55	97.7	
59	31	3.12	2.70	86.5	
60	32	2.19	2.05	93.6	
61	see above	2.51	2.41	96.0	
62	see above	2.81	2.55	90.7	

Example 63

A water-tube boiler having a heating surface area of 178 m² was cleaned with a phosphate and then by the method of the present invention.

First, the boiler operation was stopped temporarily, before cleaning, for the purpose of observing the inside of the boiler. It was found that the whole inside surface was covered with milk-white scale. The thickness of the scale was 0.5 - 1.1 mm at the upper part and 0.2 - 0.7 mm at the lower part. Analysis showed that this scale comprised 66% hydroxyapatite and 13% calcium silicate.

After the boiler operation was restarted, an itaconic acid homopolymer (molecular weight 4,500) was continuously supplied to the water at a rate of 35 mg/l. After more than one month the operation was discontinued for further observation. A small amount of scale resided in the vicinity of the water supply inside pipe of the upper part, but no scale was observed on the lower wall.

Example 64

A fire-tube boiler having a heating surface area of 37.5 m², which had not been treated with chemicals for three years, was unlocked. It was observed that the whole inside surface was covered with white scale to a thickness of 0.6 - 1.7 mm.

This scale was analysed and found to comprise 45% calcium carbonate, 35% calcium silicate, 15% magnesium silicate and 5% other materials. The boiler operation was restarted and 75% of sodium polyitaconate and 25% of sodium polyacrylate were added continuously at a rate of 75 mg per litre of the water. After one month the boiler operation was discontinued. No scale was found on the drum, fire tubes or smoke tubes.

CLAIMS

1. A method of removing scale deposited on a surface in contact with water, which comprises adding to the water a descaling agent comprising an itaconic acid polymer derived from 75 to 100 mol % itaconic acid and 0 to 25 mol% of another unsaturated monomer.

2. A method according to claim 1, in which the amount of any other monomer is less than 10 mol %.

3. A method according to claim 1 or claim 2, in which the itaconic acid polymer is a copolymer.

4. A method according to claim 3, in which the another monomer comprises an unsaturated carboxylic acid.

5. A method according to claim 4, in which the carboxylic acid is selected from acrylic acid, methacrylic acid, maleic acid, maleic anhydride and fumaric acid.

6. A method according to any of claims 3 to 5, in which the another monomer comprises an unsaturated sulfonic acid.

7. A method according to claim 6, in which the sulfonic acid is selected from vinylsulfonic acid, acrylicsulfonic acid and methacrylicsulfonic acid.

8. A method according to any preceding claim, in which the itaconic acid polymer is in the form of a water-soluble salt.

9. A method according to claim 8, in which the salt is an alkali metal salt.

10. A method according to any preceding claim, in which the itaconic acid polymer has a molecular weight of from 1,000 to 200,000.

11. A method according to any preceding claim, in which the descaling agent additionally comprises an acrylic polymer which is added in admixture, or concurrently, with the itaconic acid polymer.

12. A method according to claim 11, in which the acrylic polymer is derived from 50 to 100 mol % of acrylic acid or methacrylic acid and 0 to 50 mol % of another unsaturated monomer.

13. A method according to claim 11 or claim 12, in which the weight ratio of the itaconic acid polymer to the acrylic polymer is 100: 5-1,000.

14. A method according to any preceding claim, in which the amount of the descaling agent added to the water is from 1 to 1,000 mg/l.

15. A method according to claim 1, substantially as described in any of Examples 4 to 8, 11, 14, 15, 18, 21, 22, 25, 28 to 34, 38 to 42, 45, 48, 49, 52, 53 and 56 to 64.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.